

High-Resolution Infrared Spectrum of Diazirine, H_2CN_2 . Rovibrational Analysis of the Methylene Deformation Band

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The infrared spectrum of diazirine has been recorded at Doppler resolution with a high information Fourier transform spectrometer. The ν_3 fundamental has been reinvestigated and the overall assignment of the rovibrational transitions has been carried out. From the least-squares analysis a more accurate set of molecular constants including the sextic centrifugal distortion constants has been determined for the level $\nu_3 = 1$ and will be reported here. The higher resolution achieved here allowed the assignment of weaker lines and many Q branch transitions. Moreover many blended lines have now been resolved and could be properly assigned.

1. Introduction

Of the seven possible isomers of diazomethane, diazirine is the only one known experimentally with a cyclic structure. The diazirine ring system is unique in that it contains an azo bond in a strained three-membered ring. In the last years many aspects of the chemical properties of diazirine have been investigated [1]; However, until recently very little information was available from molecular spectroscopy.

The infrared spectra of diazirine and its isotopomers $\text{H}_2^{13}\text{CN}_2$, $\text{H}_2\text{C}^{15}\text{N}_2$, and D_2CN_2 have been recorded with a Fourier transform spectrometer at medium resolution, and the assignment of the fundamental vibrational modes has been made [2]. A rovibrational analysis of the ν_3 and ν_7 fundamentals has been carried out [2–4]. The high-resolution Fourier transform infrared spectra of diazirine and its isotopomers containing carbon-13 and deuterium have also been recorded and the bands covered successively analyzed [5–7]. In the meantime, a precise set of ground state molecular constants has been obtained from the analysis of the microwave and millimeter wave rotational spectra of diazirine [8].

The availability of these precise data induced us to reanalyze the ν_3 fundamental of the parent species in order to obtain a more accurate set of molecular constants. Furthermore, in the Doppler-limited spectrum the number of superpositions of many individual lines is drastically reduced, and the subbranches can now be assigned without ambiguity.

This paper presents the results of this reinvestigation. From the overall assignment of the rovibrational transitions of this methylene deformation mode a set of molecular constants including the sextic centrifugal distortion constants has been obtained and will be reported here.

Experimental Procedures

Diazirine was prepared by means of a modification of the method of Ohme and Schmitz, which is described elsewhere [2, 8, 9].

The Doppler-limited spectrum of diazirine was recorded in the range $1000\text{--}2750\text{ cm}^{-1}$ using the Fourier transform infrared spectrometer at the Laboratoire d'Infrarouge in Orsay [10]. The spectrum was recorded with a multipass cell containing 0.5 mbar of diazirine and with the pathlength set at 20 m. The optical section and the cell compartment were evacuated during the recording of the interferograms. The spectrum was calibrated using internally recorded H_2O and HDO lines [11, 12].

The calculations relative to the least-squares analysis were carried out on a CRAY X/MP 48 computer system. All the other computations, simulations and graphical aids were performed interactively on a CDC Cyber 180/860 A computer system using as a smart graphical terminal an IBM PC/AT microcomputer.

Rovibrational Analysis

The ν_3 fundamental vibration, centered at 1459 cm^{-1} , is of symmetry species A_1 in the molecular

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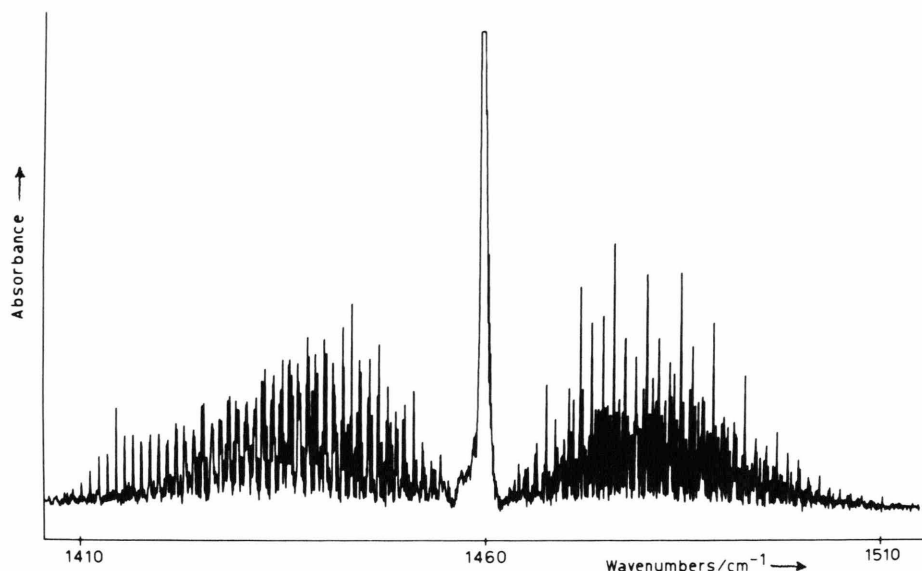


Fig. 1.
The infrared spectrum
(medium-resolution)
of the ν_3 fundamental
of diazirine, H_2CN_2 .

point group C_{2v} to which the diazirine molecule belongs. It presents a pure A-type band contour and may be approximately described as a CH_2 deformation mode.

The medium-resolution infrared spectrum in the region covered by the rovibrational structure of the ν_3 band is shown in Figure 1. The spectrum exhibits a strong Q branch and, due to the high asymmetry of the molecule ($\alpha = -0.427$), the P and R branches do not present any regular pattern.

For the least-squares analysis the Hamiltonian employed for the computation of the rotational energy levels in the ground state and in the vibrational state $\nu_3 = 1$ is Watson's A reduction in the I' representation [13]:

$$\begin{aligned} H = & 1/2(B + C) \mathbf{P}^2 + [A - 1/2(B + C)] \mathbf{P}_a^2 \\ & + 1/2(B - C)(\mathbf{P}_b^2 - \mathbf{P}_c^2) - \Delta_J \mathbf{P}^4 \\ & - \Delta_{JK} \mathbf{P}^2 \mathbf{P}_a^2 - \Delta_K \mathbf{P}_a^4 - 2\delta_J \mathbf{P}^2 (\mathbf{P}_b^2 - \mathbf{P}_c^2) \\ & - \delta_K [\mathbf{P}_a^2 (\mathbf{P}_b^2 - \mathbf{P}_c^2) + (\mathbf{P}_b^2 - \mathbf{P}_c^2) \mathbf{P}_a^2] \\ & + \Phi_{JK} \mathbf{P}^4 \mathbf{P}_a^2 + \Phi_{KJ} \mathbf{P}^2 \mathbf{P}_a^4 \\ & + 2\phi_J \mathbf{P}^4 (\mathbf{P}_b^2 - \mathbf{P}_c^2) + \phi_K [\mathbf{P}_a^4 (\mathbf{P}_b^2 - \mathbf{P}_c^2) \\ & + (\mathbf{P}_b^2 - \mathbf{P}_c^2) \mathbf{P}_a^4], \end{aligned}$$

where $\mathbf{P}$, $\mathbf{P}_a$, $\mathbf{P}_b$, and $\mathbf{P}_c$ are the operators of the total angular momentum and its components along the principal inertial axes a , b , c . The coefficients A , B , and C are Watson's A -reduced rotational constants, the parameters Δ_J , Δ_{JK} , Δ_K , δ_J , and δ_K are the quartic and Φ_{JK} , Φ_{KJ} , ϕ_J , and ϕ_K are sextic centrifugal distortion

constants. The rovibrational transition wavenumbers are given by

$$\begin{aligned} \nu_{\text{PQR}} = & \nu_0(v_l) + E(v_l = 1, J', K'_a, K'_c) \\ & - E(v_l = 0, J'', K''_a, K''_c), \end{aligned}$$

where ν_0 is the band origin and the E 's are eigenvalues of the effective rotational Hamiltonians.

For this A -type band the following selection rules were taken into account: $\Delta J = 0, \pm 1$, $\Delta K_a = 0$, and $\Delta K_c = \pm 1$. The P, Q, and R branches are then each composed by an even and an odd subbranch depending if $J'' + K''_a + K''_c$ is even or odd, respectively.

The assignment of the rovibrational transitions was done following the methods developed in previous work [2–6]. A preliminary calculation of the rovibrational transition wavenumbers, together with the relative intensity of each line, was carried out using as starting values for the excited state the molecular constants determined from the analysis of the medium-resolution spectrum [2], and for the ground state, the molecular constants obtained from the rotational analysis [8]. Then, for each K_a , a correlation diagram was made of the deviation of the computed wavenumbers from the experimental positions of the peaks of the spectrum for increasing J' [14]. The P and R branch transitions to the same excited rovibrational level form series of pairs of points which can be easily recognized on these diagrams.

Keeping the molecular constants for the ground state fixed, the constants for the level $\nu_3 = 1$ were re-

Table 2. Molecular constants (all parameters in cm^{-1}) in Watson's A -reduced Hamiltonian for the ν_3 fundamental mode of diazirine^a.

	Ground State ^b	$\nu_3 = 1$	
A	1.36598990	1.36955	1.3695536 (21)
B	0.789478838	0.786797	0.78682361 (66)
C	0.55792309	0.5587946	0.55881720 (60)
$\Delta_J \times 10^6$	1.05290	1.008	1.06921 (27)
$\Delta_{JK} \times 10^6$	3.6005	3.83	3.5616 (37)
$\Delta_K \times 10^6$	-0.7824	-0.7824	-0.5885 (85)
$\delta_J \times 10^6$	0.31491	0.293	0.31185 (37)
$\delta_K \times 10^6$	2.5744	2.47	2.6318 (15)
$\Phi_{JK} \times 10^{10}$	-0.188	0	-0.216 (27)
$\Phi_{KJ} \times 10^{10}$	0.93	0	0.84 (11)
$\varphi_J \times 10^{12}$	-0.36	0	-0.56 (13)
$\varphi_K \times 10^9$	0.11	0	0.1345 (92)
ν_0	—	1459.1506	1459.134380 (89)
σ	—	0.0173	0.0012
Reference	[8]	[2]	This work

^a Figures in parentheses are standard deviations in units of the least significant figures.^b Ground state constants held fixed during the fit.

finer, and the above procedure repeated with successively larger sets of assigned transitions with increasing K_a and J values.

Due to the high resolution of the spectrum, the range of the differences between observed and computed wavenumbers to be taken into account could be reduced by a factor of 10 compared to the analysis of the medium resolution spectrum; in this way it was possible to have, in each K_a diagram, only one well defined series.

Several transitions belonging to the Q branch could also be inserted into the assignment and fitting procedure.

In Table I*, the observed values of the assigned transitions included in the least-squares analysis are reported, together with the difference between these values and those computed from the final set of molecular constants. The observed-calculated error for each line is consistent with the instrumental resolution. More than 2200 rovibrational transitions were assigned up to $K_a = 20$ and $J = 47$, and of them, 2040 were included in the fit.

In Table II, the molecular constants obtained by the least-squares analysis are reported, together with the constants determined from the previous analysis of the medium resolution spectrum. All the rotational and quartic centrifugal distortion constants are fully

determined, and four of the sextic constants, in view of their small values, are reasonably determined. The standard deviation of the fit is compatible with the resolution of the spectrum.

Figure 2 shows a portion of the P branch at high resolution together with the Fortrat diagram showing the assignment of selected P(J'') transitions ($\Delta K_a = 0$, $\Delta K_c = -1$). In the Fortrat diagram, the lines connect the transitions (marked with symbols) which have the same J'' value. It can be seen that at high K_a values, the transition wavenumbers of both the even and odd subbranches have the same values, as a consequence of the degeneracy of the rotational energy levels in the first excited vibrational state.

The same kind of diagram for a portion of the R branch is shown in Fig. 3, together with the relative high-resolution spectrum. In this case the shape of the plots relative to the R(J'') transitions ($\Delta K_a = 0$, $\Delta K_c = 1$) presents a particular pattern which explains the clusters of lines found in the R branch region of the spectrum.

The availability of high-resolution data in this study means that many more lines could be fitted compared to the medium-resolution analysis of the ν_3 band of diazirine, so that the constants determined here are considerably more accurate. In addition, the graphic assignment methods employed are more useful with fully resolved lines, so that no reliance on the simulated spectrum was necessary in evaluating the assignment.

* Available from A.G upon request.

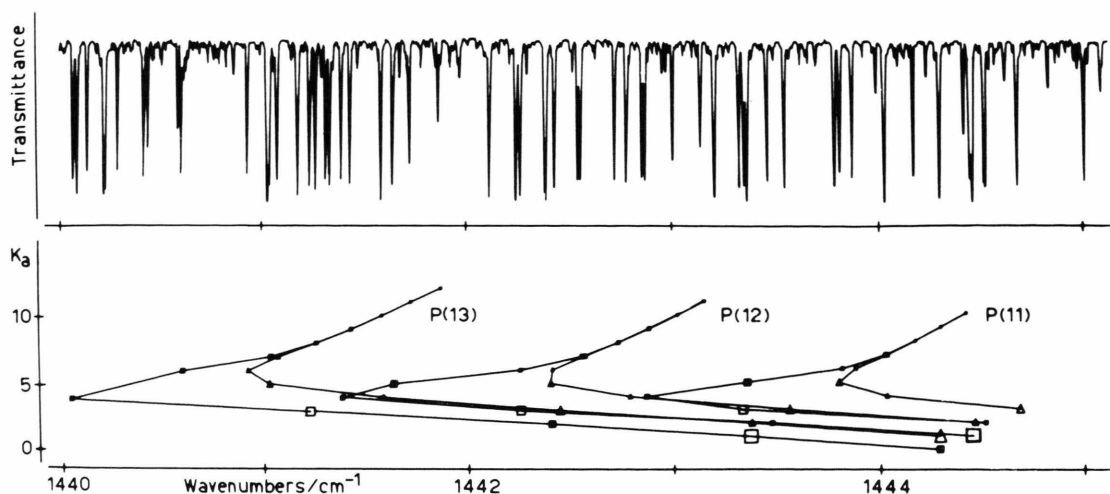


Fig. 2. High-resolution spectrum of the ν_3 fundamental in diazirine. Portion of the P-branch region with the Fortrat diagram showing the assignment (see text). The symbols $\square$ and $\triangle$ represent the even and odd subbranches, respectively; the size of the symbols is proportional to the relative intensities of the lines.

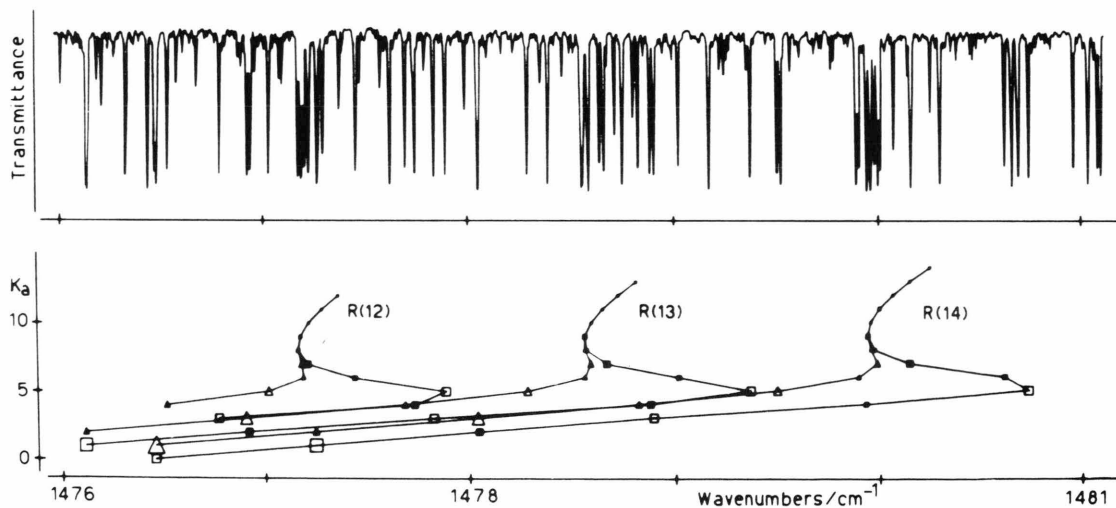


Fig. 3. High-resolution spectrum of the ν_3 fundamental band in diazirine. Portion of the R-branch region with the Fortrat diagram showing the assignment; see text and caption to Figure 2.

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